REVIEW

Photocatalytic membrane filtration and its advantages over conventional approaches in the treatment of oily wastewater: A review

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ABSTRACT

Clean water supply has become one of the biggest challenges of the 21st century; therefore, water source protection is of increasing importance. Beyond environmental protection reasons, economic concerns—derived from increasing costs of processing water and wastewater discharge—also prompt industries to use advanced wastewater treatment methods, which ensure higher purification efficiency or even the recycling of water. Therefore, highly effective treatment of oily wastewaters has become an urgent necessity because they are produced in high quantities and have harmful effects on both the environment and human population. However, high purification efficiency can be difficult to achieve, because some compounds are hard to eliminate. Conventional methods are effective for the removal of floating and dispersed oil, but for finely dispersed, emulsified and dissolved oil advanced methods must be used, such as membrane filtration which exhibits several advantages. The application of this technology is restricted by fouling—the major limiting factor—which jeopardizes the membrane performance. In order to reduce fouling, in-depth research is being conducted to make the treatment of oil-contaminated water technically and economically feasible. The present work aims to review the conventional oil separation methods with their limitations and to focus on membrane filtration, which ensures significantly higher purification efficiencies, including the main problem: the flux reduction caused by fouling. This paper also discusses promising solutions, such as membrane modification methods, mostly with hydrophilic and/or photocatalytic nanoparticles and nanocomposites, overviewing the efforts that are being made to develop feasible technologies to treat oil-contaminated waters.

KEYWORDS
membrane fouling, modified membrane, oil contamination, oil-in-water emulsion, photocatalytic membrane

1 | INTRODUCTION

Large amounts of oily wastewaters are produced by many different industries, such as oil refining, oil storage, transportation, metal, lubricant, oil, petroleum, and food industries.[1–3] The treatment of oily wastewater is necessary because its contaminants can negatively affect both the ecosystem and human population, lowering the quality of superficial and groundwater, compromising aquatic lives and human health, affecting the quality of soil and crop production, and polluting the atmosphere with volatile contaminants.[4–6] In addition, there are economic reasons—derived from increasing costs of water processing and wastewater discharge—that make the development of efficient treatment methods necessary, while also ensuring high purification efficiency or even water recycling. It is difficult to carry out this task due to several inorganic and organic substances, that is, dissolved minerals, dispersed and emulsified oils, and dissolved organic compounds, gases, and traces of chemicals used in the industries.[7,8]

The treatment of oily wastewater can be carried out by conventional methods, such as skimming,[9,10] flotation,[11,12] chemical destabilization using coagulation/flocculation methods,[13,14] electrocoagulation,[9,15,16] centrifugation,[5,17] and biological treatments.[18] These are effective for the elimination of floating oil ($d > 150\,\mu m$) or even dispersed oil ($d > 20\,\mu m$), but for finely dispersed, emulsified, and dissolved oily contaminants, advanced methods must be used. Membrane filtration is a promising method to treat these kind of pollutants due to several advantages like easy integration, and high removal efficiency.[6,19,20] With the combination of one or more conventional methods and membrane filtration, the desired high purification efficiency can be achieved. Nowadays, the treatment tend to still be too expensive and/or too time-consuming,[21] because the major limitation to the application of membrane-based oily wastewater treatment is fouling, that causes severe flux decline and reduces membrane performance.[8,21–23] Besides, regular filtration shutdowns—to clean the membrane and recover the permeability—increase the costs and complexity of the system. The chemicals used for cleaning the membrane surface also increase the costs and reduce membrane performance and lifespan.[24]

Researchers all over the world carry out in-depth investigations into possible solutions to make the method both technically and economically feasible. In order to reduce the disadvantages, it is necessary to use appropriate pretreatments and/or increase membrane hydrophilicity to decrease the fouling properties.[25] Based on this, the development of ultra-hydrophilic membranes with structures containing nanomaterials is revolutionizing the separation of oily wastewater by avoiding the attachment of oil droplets on the surface and stabilizing the filtration resistance at a low level, resulting in membranes without significant fouling properties.[6,26,27] Photocatalytic nanomaterials promise further advantages for the preparation of highly hydrophilic, self-cleaning membranes, as these materials can decompose not only the organic pollutants from the surface when activated by artificial or solar irradiation[28,29] but also the organic contaminants of the fouled pores as well, converting them into small (or even nontoxic) substances—without the formation of secondary pollutants.[28–30] The most widely investigated photocatalytic material is titanium dioxide (TiO_2) due to its low cost, availability in large quantities, high chemical stability, and photocatalytic activity, etc.[31] However, despite the numerous advantages of TiO_2, it can be activated mainly by ultraviolet (UV) light, which makes up a small fraction of solar light; therefore, solar systems that use only pure TiO_2 have limited efficiency in the degradation of hydrocarbons.[32] Considering this, and the fact that artificial UV-light-based activation needs significant electrical energy, the development of visible-light active photocatalytic materials and their use in the preparation of solar-light active membranes has a huge potential to achieve high efficiency during pollutant removal and/or membrane surface cleaning.[33] Solar-light active superhydrophilic photocatalytic membranes could be the future's novel solution for advanced oil-in-water emulsion separation as they will be able to minimize the fouling problems, and be cleaned in a chemical- and energy-free manner, by simple solar light irradiation.

The present work aims to provide an overview of the characteristics and effects of oily wastewaters and their suitable treatments, starting with conventional methods explaining their advantages and disadvantages. This study also deals with the membrane filtration process and its limitations related to flux reduction and fouling problems. The possible solutions, that is, modified membranes and the development of hydrophilic nanomaterials, to enhance membrane performance are described in detail. Furthermore, photocatalytic nanocomposite-modified membranes are also discussed as future perspectives.

2 | SIGNIFICANCE OF TREATING OILY WASTEWATERS

Oily wastewaters consist of mainly oil, salt, and surfactants, but they also contain numerous harmful compounds: saturated straight-chain and branched hydrocarbons, cyclic hydrocarbons, olefins, aromatic hydrocarbons, and other non-organic substances, such

as sulfur- and nitrogen-containing compounds, and heavy metals.[8,34,35] The damage caused by oil-contaminated waters depends on the type, volume, and quality of the polluting oil, but also on the place and conditions of the discharge. Oily wastewaters can have harmful effects on organisms due to coating, asphyxiation, poisoning, or causing sublethal and stress effects, reducing the abundance and diversity of the fauna and flora.[36] Soils can also be affected by oil contamination, reducing bacterial activity, killing earthworms, reducing plant growth, affecting root elongation, and germination,[37] which also affects crop production and groundwater quality.[4,5] In relation to animals and human beings, effects of oil contamination can range from acute symptoms to chronic diseases, and by the accumulation in food chain, it can cause DNA damage, genotoxic, carcinogenic, and mutagenic effects, where the possible consequences include allergies, respiratory problems, autoimmune disorders, spontaneous abortion, or even cancer.[34,38,39] There are regrettable examples, where nature has been severely damaged by years of oil contamination, and most of the population has been constantly exposed to crude oil through the water, air, and soil, and the number of degenerative diseases increased and life expectancy decreased.[34,40] These examples highlight the importance of developing efficient oily wastewater treatments.

3 | UTILIZATION OF CONVENTIONAL TREATMENTS FOR THE ELIMINATION OF OILY COMPOUNDS

To reduce the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in oily wastewaters, the most common methods are skimming, centrifugation, flotation, and chemical destabilization. Biological decomposition, which uses anaerobic and aerobic bacteria, must also be listed here as it is a conventional wastewater treatment method; however, it is a novel and dynamically developing technique in this field. These conventional methods are often not efficient enough to achieve the newest limit values of treated wastewater, due to the complexity of the mixture and the presence of emulsified/dissolved oil and/or non-biodegradable organic contaminants.[5,21,41,42] But, due to low operation costs and high purification efficiency in the case of floating/dispersed oils and biodegradable organic compounds, highly efficient combined treatments usually start with (or contain) one or more of these methods as pretreatment(s).[43,44]

3.1 | Skimming

One of the most conventional oil separation method is skimming, a simple gravity separation method based on the density difference between the oil and water, in which the oil rises to the top of the device, and the suspended solids sink to the bottom of the separator.[45] The API tank—designed according to American Petroleum Institute standards—is a widely used and simple separator that can eliminate droplets bigger than 150 μm.[46] There are parallel and/or corrugated plate separators that can enhance gravity separation and remove oil droplets bigger than 50 μm.[47] However, these skimming devices generate a large amount of sludge and are not efficient at eliminating the finely dispersed and dissolved oil, which makes it necessary to combine this method with other treatments.

3.2 | Centrifugation

Centrifugal forces can be utilized to increase the flow rate and/or purification efficiency, which can be achieved using centrifuges or hydrocyclones. The advantages of centrifugal separation are high throughput capacity, smaller equipment, and shorter residence time compared with simple gravity separation.[10,14] During the application of this method, two forces are acting on the oil droplets: (a) buoyancy, which is responsible for the upward movement of the droplet as a result of the density difference between oil and water, and (b) drag force, which opposes buoyancy until the rise velocity reaches a terminal value when the two forces are equal.[10] This terminal velocity is used as a separator design criterion and determines the droplet sizes that can be separated at a given resident time and throughput capacity.

According to Benito et al.,[14] centrifugation can be used to treat both mineral and semi-synthetic oil containing water with >90% purification efficiency; however, the treated water still can still contain up to 1500 mg/L oil. Separation efficiency can be improved by increasing the buoyancy force and/or the droplet diameter.[10] These aims can be achieved by coagulation/flocculation methods and bubble production-based flotations, which are detailed in the following sections.

In contrast with conventional centrifuge machines, hydrocyclones have no moving parts, just a cylindrical and a conical part. The fluid is injected tangentially through the inlet in the upper part, resulting in strong swirling motion and therefore, high centrifugal forces. As the fluid passes through in a spiral fashion, dense particles are forced against the wall and migrate downwards to the underflow; meanwhile, fine or low-density

particles move upward to the overflow. Despite their advantages, hydrocyclones have low separation efficiency when the dispersed oil droplet diameter is smaller than 15 μm.[48] In order to increase the oil removal efficiency, special hydrocyclones have been developed, such as the bubble enhanced hydrocyclone, in which the oil droplets and the bubbles collide with each other, and thus are carried out of the cyclone.[48]

3.3 | Chemical destabilization

Chemical destabilization involves the usage of chemicals (coagulants and flocculants) to neutralize the surface of colloids and to agglomerate them into bigger particles and flakes, which can be more easily removed by other separation techniques such as skimming or flotation. This method is widely used to treat wastewater because of its simplicity, low-energy consumption, easy operation, and versatility.[13,49] The most widely used coagulants for the treatment of oily wastewaters are aluminum sulfate, ferric chloride, and polyaluminum chloride,[17,42,50,51] but the development of novel, more efficient, and cost-effective coagulants is also an important field of research. For instance, Zeng et al.[52] combined a coagulation/flocculation system with polyzinc silicate and anionic polyacrylamide to remove oil from heavy oily wastewater and removed more than 99% of the suspended solids and oil. Zeng and Park[53] observed higher coagulation/separation performance by using zinc silicate and anionic polyacrylamide, compared with conventional coagulants. According to the authors, the addition of zinc more favorably neutralizes charges of the colloidal particles in oil-contaminated water, more effectively reduces turbidity, suspended solid content, and COD in a broader pH range.

Electrocoagulation is also a possible method to treat oily wastewaters, which requires smaller amounts of reagents compared with conventional coagulation, forming a smaller volume of sludge.[15,54] The process is based on the in situ generation of coagulants by electrically dissolving aluminum or iron ions, which then attract fine, negatively charged droplets and particles. Due to the reduced surface charges and resulting coalescence of the droplets, they can be easily separated.[50] The metal ions are generated at the anode, and hydrogen gas is released from the cathode. Hydrogen gas also helps to float the flocculated particles to the top of the water.[55] According to Öğütveren et al.,[16] this method can be effective to destabilize oil-in-water emulsions and the use of aluminum is more effective and requires less energy.

3.4 | Flotation

Flotation is a process that uses air bubbles to adhere the dispersed particles or oil droplets to the water and raise them to the surface with high efficiency, due to the significant density difference between the water and bubbles. Conventional flotation techniques can be divided into three different types:

- electro-flotation (EF), which generates micro-bubbles by passing direct current between two electrodes electrolyzing the water[56];
- dispersed (induced) air flotation (IAF), which generates bubbles mechanically by combining a high-speed mechanical agitator with an air injection system[11]; and
- dissolved air (pressure) flotation (DAF), in which the bubbles are formed by a pressure increase followed by a pressure reduction of the water stream.[57]

Flotation has shorter retention time, higher loading rate, and higher efficiency than simple coagulation, and it is widely used to purify oily wastewaters. Because oil droplets easily adhere to air bubbles and have lower density than water, therefore, fast separation and reduced sludge production can be achieved.[11] However, the presence of emulsified and very fine (submicron or nanoscaled) oil droplets makes the phase separation challenging even during flotation, which requires very fine bubbles, quiescent hydrodynamic conditions, or the addition of emulsion-breaking chemicals prior to flotation, resulting in an increase in its complexity, time, and cost.[12]

The utilization of hybrid systems, such as coagulation or flocculation with IAF or DAF, can also be beneficial and has been analyzed by several authors.[12,51,58]

3.5 | Biological treatments

Biological treatments use microbes such as genera *Mycobacterium*, *Nocardia* *Corynebacterium*, and *Rhodococcus*[59,60] to decompose hydrocarbons and colloidal organic pollutants with four crucial processes: hydrolysis, fermentation, acetogenesis, and methanogenesis in aerobic or anaerobic conditions. During these processes, the pollutants can be transformed partly into harmless and stable substances.[5,58] This method can be a cheap and simple solution; however, oily contaminants have high toxicity and contain poor nutrients and thousands of different organic compounds (saturates, aromatics, asphaltenes, and resins), and not all of them can be decomposed efficiently—for example, high-molecular-weight polycyclic aromatic hydrocarbons may not be

degraded at all.[18,61,62] Kis et al.[63] isolated a novel *Rhodococcus* sp. MK1 to degrade various hydrocarbons found in diesel oil. Although the new microorganism is adaptive and could decompose numerous components in liquid or solid phase under laboratory conditions, there were difficulties in the ex situ study.

New techniques are being investigated to increase the efficiency of oily wastewater treatment, for example, membrane bioreactor,[64] up-flow anaerobic sludge blanket,[18] and biological aerated filter reactor.[65] To date, these technologies alone are not capable to achieve the currently required standards; therefore, biological treatments must also be supplemented with other method(s).

4 | MEMBRANE FILTRATION TO ACHIEVE HIGHER PURIFICATION EFFICIENCIES

After the application of the previously detailed conventional methods, wastewaters often still contain significant amounts (few to hundreds of mg/L) of microscale and/or nanoscale oil droplets, requiring further treatment before discharge or reuse. Membrane filtration can be a good choice because it minimizes additional costs, it does not require chemical additions, it is easy to handle, its energy requirement is low, and it can still reach high removal efficiency.[8,19,20,22,66] Therefore, this process is more frequently used to treat oily wastewater and to overcome the deficiencies of previously mentioned conventional methods.

During membrane filtration the membrane separates the contaminants from the water with a physical barrier that allows water to flow through the membrane, while the other substances are retained by the membrane surface. The water crosses the membrane due to a driving force, such as concentration difference, electric potential, partial pressure, or hydraulic pressure. The membrane separation behavior depends on adsorption, sieving, and electrostatic phenomena.[1,19,67] In general, membrane separation by itself is effective to remove (oily) contaminants, but it is beneficial to minimize the accumulation of them on membrane surfaces to provide higher fluxes, so conventional methods combined with membrane filtration can be used, such as flocculation with membrane microfiltration (MF),[68] or filtration and centrifugation followed by ultrafiltration (UF).[14] Another technique to increase the membrane filtration efficiency is to combine different membrane processes, such as MF with UF or UF with reverse osmosis (RO), etc.[5]

Although some applications are already well developed, several challenges still need to be addressed in order to improve the currently available membranes'

characteristics in terms of separation performance, antifouling properties, and long-term stability.[1]

4.1 | Types of membranes

Membrane filtration processes can be characterized according to the pore size or molecular weight cut-off (MWCO) value that defines the size of particles/droplets/molecules/ions, which are retained by the membrane surface. This value decreases from MF to UF (UF), nanofiltration (NF), and RO, and the hydrodynamic resistance for water to pass through the barrier increases in this order.[19,20]

MF is usually used when the aim is to remove bacteria, suspended soils, or substances with sizes between 0.1 and 10 μm.[19,69] László Kiss et al.[70] used an MF membrane to separate the oil content of an oil-in-water emulsion and achieved higher retention rates in the case of relatively high oil concentration. Nandi et al.[71] used a low-cost MF membrane and removed 98.8% of the oil. Wang et al.[72] used MF membrane to treat oily wastewater and recovered the membrane with simple cleaning, and aeration at regular intervals significantly improved performance. Currently, by using MF, satisfactory water purity can be achieved when it is combined with other technologies or when the water contains low concentrations of oil compounds.[21,73]

UF can separate particles of 0.001–0.1 μm, macromolecules, and colloids from water; however, most of the dissolved ionic species still pass through the membrane. The application of UF to separate oily compounds has been widely studied and shows high efficiency in total organic carbon (TOC) removal and can achieve up to 98–99% of oil removal.[8,19,69,73] Bodzek and Konieczny[74] investigated a UF tubular membrane to treat oil emulsion and, with the pre-elimination of suspended oil, they achieved 99% COD removal efficiency. Srijaroonrat et al.[25] used a UF membrane to treat oil-in-water emulsions, applying cyclic backflushing to recover the original performance and measured 50–120% higher steady-state fluxes (depending from the used transmembrane pressure) by using very brief (0.7 s) backflushing every minute.

NF can separate divalent ions, small organic molecules, and inorganic molecules with a size of 0.0005–0.001 μm. Therefore, this method is commonly used in desalting procedures, drinking water generation, textile and paper industry, etc. The rejection of solutes can achieve >99% efficiency.[19,21,69] Among the various types of membrane separation processes, RO is the one which can eliminate even the finest molecules except water. It requires larger amounts of energy compared with the others, because water molecules have to be

pushed through the membrane against a high osmotic difference with a high-pressure pump.[21] The disadvantages of NF and RO—when treating oily wastewater—compared with MF and UF, are the higher fouling tendency, more difficult fouling recovery, and lower fluxes.[1] These technologies can be used if the salt content is high in the oily wastewater.[41]

4.2 | Materials of membranes

To treat oily wastewater, organic (polymeric) and inorganic (ceramic) membranes can also be used for the effective removal of oil compounds.[8,20,22]

Polymeric membranes consist of two layers: a highly porous support layer that provides resistance and strength, and a relatively thin and less porous membrane layer of the same—or sometimes a more appropriate—material, where the separation happens.[20] Cellulose acetate (CA) membranes are widely used because of the low cost, easy handling, and low fouling propensity, but their disadvantages are their limited operating temperatures and pH ranges.[28] To maintain excellent permeability, selectivity, and stability, numerous authors used different polymeric membranes, such as polypropylene (PP),[75] polyvinylidene fluoride (PVDF),[43,72] polytetrafluoroethylene (PTFE known as Teflon),[70] polyethersulfone (PES),[76] polysulfone (PSf),[77] and polyacrylonitrile (PAN).[78] Polymeric membranes are synthetic and can be used to separate oil from water. They have numerous advantages, such as the possibility to control the density, size, size distribution, shape, and vertical alignment of membrane pores,[8,21,79] besides their high efficiency at removing emulsified and dispersed oil, their low energy requirement, and cost.[1,20] Nonetheless, their disadvantages, such as fouling tendency and quick flux decrease, make the use of these membranes difficult for treating oily wastewater in large scale. Therefore, many studies focus on possible solutions to decrease the disadvantages and improve the hydrophilicity and antifouling properties of these membranes.[6,76,80–82]

Ceramic membranes usually have asymmetric structure composed of two or three layers: (a) a few-millimeter-thick support layer that provides the membrane's mechanical strength (this layer usually contains relatively large pores: 1–10 μm), (b) an optional 10- to 100-μm-thick intermediate layer, and (c) a top layer (with the desired pore size) that provides the membrane's selectivity.[83,84] The main synthesis procedures of inorganic membranes are slip casting, chemical vapor deposition, *sol-gel* processes, and pyrolysis.[21,22,84] The pore size and characteristics of the upper selective region are chosen according to

the grain size and the given particle type.[20,85] The mechanical, thermal, and chemical stability of inorganic membranes makes them suitable to treat industrial and hazardous wastewaters and also enables the superior cleaning of the fouled membranes with different chemicals.[8,21] There are some disadvantages of conventional ceramic membranes, like difficulties with sealing, and that they need sensitive handling.[21,26] Moreover, fouling by oily contaminants is a serious problem, due to the significantly reduced flux, efficiency, and lifetime.[8,22,86,87] Nevertheless, despite the advantages of ceramic membranes, they are still relatively expensive for large-scale membrane applications and their use is often limited to relatively small-scale industrial separations.[20,87] Compared with polymeric membranes, ceramic membranes are more tolerant to organic solutions, resistant to corrosion, and reliable under harsh operating conditions, for example, high temperatures, high surface shear rates, or presence of oxidative solvents, and it is easier to remove the fouling layer.[20,83]

Despite all the efforts to improve both ceramic and polymeric membrane efficiency for oil removal, fouling is still the major limiting factor of the application of membrane-based oily wastewater treatment.[8,21,22]

4.3 | Fouling problems

Fouling is the result of contaminant accumulation on the membrane surface and in the pores during the filtration. It is caused by organic colloids, organic macromolecules (organic fouling), inorganic suspended solids (inorganic fouling), soluble inorganic compounds (scaling), and by living/growing microorganisms (biofouling).[6,46,83,88] In the case of oil-contaminated waters, scaling is caused by the precipitation of salts and hydroxides, and the blockage of the surface and the fouling of the pores are caused mainly by oil droplets.[46] The fouling layer can be affected by the characteristics of the feedwater such as concentrations and physicochemical properties; membrane properties like surface roughness, charge properties, and hydrophilicity; and operational conditions such as flow velocity, applied transmembrane pressure, recovery, and temperature.[21,23] The fouling mechanism is determined mostly by the electrostatic and van der Waals interactions between the colloidal particles and the membrane surface, and it is also influenced by the same interactions between the particles.[89–91] In the case of oil-contaminated water, droplet size, ionic strength, temperature, pH, and emulsifier concentration also affect these interactions between the membrane surface and the contaminants.[92,93] It is important to study the variation and dependence of these conditions because they can affect

the membrane pore, efficiency, fouling, and performance. Much research is being conducted in order to discover the relationship between the characteristics of water and treatment,[35,94] by developing kinetic models,[95] quantifying kinetic rates for different compounds (e.g., surfactants),[96] understanding the interactions between the constituents of the oily wastewater,[97,98] etc.

Oily contaminants can quickly form a hydrophobic layer acting as a significant water barrier on the membrane surface, which causes severe flux decline, reduced productivity, decreased membrane performance, decreased life span, and difficult cleaning, which can increase the energy consumption and treatment cost.[23] Much research is being carried out to overcome this problem and to make the utilization of membrane filtration feasible to treat oily wastewater.

4.4 | Available solutions for flux reduction

Possible solutions for the mitigation of membrane fouling are (a) development of improved cleaning procedures, (b) application of pretreatment, (c) membrane modification, (d) enhancement of hydrodynamic surface shearing,[83] and (e) application of backflush with air, water, or permeate.[25] The addition of suitable physical (centrifugation, flotation, etc.), chemical (destabilization, oxidation, etc.), or biological treatment(s) is also a promising way to decrease the quantity of fouling contaminants and/or their adhesion to the membrane surface.

Veréb et al.[82,99] applied ozonation before the MF of an oil-in-water emulsion and concluded that short-ozonation can increase the flux and reduce filtration resistance, due to the increased negative surface charge of the oil droplets. Chang et al.[100] applied ozonation after UF to destroy the structure of the remaining surfactants in the permeates while keeping the characteristics of the emulsion; applying such treatment, the permeate could be reused. The authors concluded that after ozonation the characteristics of the emulsion did not change, showing that ozonation enabled the reuse of permeate. Kwon et al.[101] combined surfactant-modified zeolite adsorbent with submerged membrane bioreactor to treat produced water, and they achieved 92% TOC removal and 95% volatile organic compounds removal with the combined system. Due to the combined treatment, daily brushing of the membrane surface was enough to prevent fouling and keep the flux of the system for 2 weeks. It is also possible to combine different types of membrane techniques to achieve higher oil removal efficiency and/or higher flux. Grytaet al.[43] treated bilge water with a hybrid UF/membrane distillation (MD) system, by recycling the MD retentate at high temperature to the UF plant. They achieved complete oil removal, 99.5% TOC removal, and 99.9% dissolved solid removal efficiency with the as-described system, which was due to the fact that in the MD system low oil concentration was maintained by recycling its retentate, resulting in higher efficiency. Enhanced mass driving force—as a result of the increased temperature—also contributed to the higher fluxes. After the UF plant was rinsed with permeate, 1 wt.% detergent solution, and tap water, it was possible to regenerate the flux in 98%, demonstrating the improvement of the combined system.

Another possible way to minimize flux reduction is to decrease the adhesive interactions between the foulants and the membrane surface by improving the membrane hydrophilicity. Possible methods are sulfonation, carboxylation, physical adsorption of hydrophilic compounds, grafting, plasma treatments, etc.[102–105] Among others, the use of hydrophilic materials for membrane modification is a very promising solution to avoid the attachment of oil droplets to the membrane surface and to stabilize the filtration resistance at a low level. Hydrophilicity can be characterized by the contact angle (α) between a water droplet and the membrane surface, as a lower contact angle indicates higher hydrophilicity (Figure 1).[27]
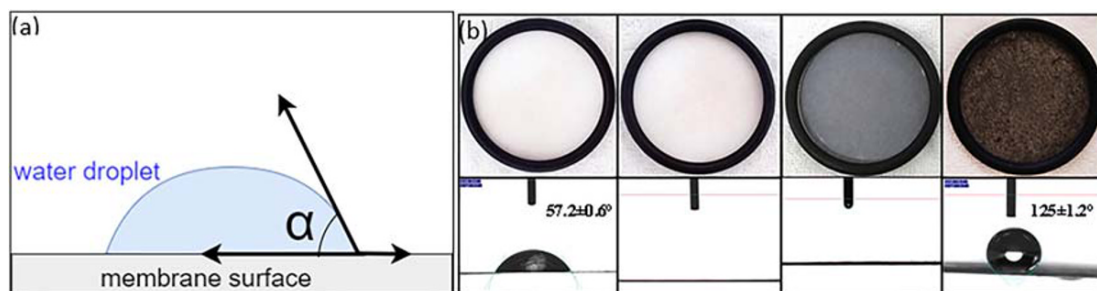

FIGURE 1 (a) Contact angle between water droplet and membrane surface (b) Contact angle between water and various modified membranes[106]

4.5 | Membrane modification

Many membrane materials are hydrophobic, which causes interference in the interaction between the water molecules and membrane surface, inhibiting water flux through the membrane. Moreover, hydrophobic membrane materials also facilitate the adherence of hydrophobic molecules on the membrane surface and consequently, increase fouling by building up on the boundary layer.[27,102] Accordingly, it is necessary to increase the hydrophilicity of the membranes by modifying their properties. The different membrane modifications groups are summarized in Table 1.[6,27,84,102,105,107] This review focuses on surface modification with physical immobilization, grafting, and blending modification, detailed in the next sections.

4.5.1 | Membrane surface modification

Membrane surface modification can be achieved through physical or chemical techniques. A very important factor is the interaction between the membrane and the modifying material. Coating materials can be simply adsorbed to the membrane surface via secondary interactions (van der Waals and electrostatic interactions and hydrogen bonding), or some materials can be cross-linked in situ onto the membrane surface enabling anchored interactions and enhanced stability. The strength of these secondary interactions depends on the nature of the polymer surface and the surface modifier. Grafting and plasma treatments are the most widely used chemical techniques[1,108] which can modify the polymer surface without affecting bulk properties. According to Ulbricht,[28] surface modification should focus on minimizing the interactions between the membrane and undesired molecules of the treated water and also on increasing the selectivity of the process.

Physical immobilization can be done, for example, by dipping the membrane into the colloidal solution of the chosen modifier compound (Figure 2a), and the resulting secondary interactions will determine the strength of the interaction between the material and the membrane.[108] In addition to hydrophilicity, surface roughness can also be modified by surface coatings, as was demonstrated by Kasemset et al.[103] They coated a polyamide RO membrane with polydopamine, and due to the reduced membrane roughness, significantly reduced fouling resistance was achieved during the filtration of oil-in-water emulsion. A significant disadvantage of physical adsorption and deposition is the possible leaching over time. Thus, many studies aim to increase the strength of the interactions between the particles and membrane to avoid losses during filtration.[27,84,109]

Surface grafting modifies the membrane by immobilizing functional chains onto its surface through covalent interactions (Figure 2b). This method provides significantly longer stability compared with physical deposition.[1,27,102] Numerous studies are based on coupling polymers or monomers. Zhao et al.[110] grafted perfluoroalkyl groups onto PAN membrane, which resulted in >99% flux recovery ratio and <13% total flux decline. Kasemset et al.[87,111] developed a ceramic-supported polymer ultrafilter membrane, which was grafted with zirconia, and they achieved 45–65% higher oil rejection rate than with the neat membrane, and no irreversible fouling was observed, whereas in the case of the neat membrane it could not be completely recovered even after rigorous cleaning.

4.5.2 | Blending modification

Blending modification is widely used for polymeric membranes because it is a simple, versatile, and cheap procedure. It is also efficient for achieving the desired properties of the membrane. This method is used mainly during the preparation of membranes via phase inversion that transforms the polymer from liquid to solid state in a controlled way in a selected solvent, thus distributing the polymer uniformly. The chosen modifying material can be added to the polymer casting solution in order to fabricate the modified membrane (Figure 2c).[26,27]

Arthanareeswaran et al.[112] prepared polyethylene glycol (PEG) blended PSf membrane, and they found that due to the utilization of PEG, higher membrane porosity and consequently higher flux were achieved. Moreover, higher PEG concentrations resulted in delayed compaction. Pagidi et al.[77] also blended a PSf membrane with four different polymeric additives (PVP, PEI, PEG, and PES) to use them for the treatment of oil-in-water emulsions. The hydrophilicity, flux, and oil retention ratios were also increased by all the investigated additives, which were explained by the reduced gel layer formation, due to the modified surfaces. In this study, the PSf/PVP membrane had the best performance, with the highest oil retention ratio and flux. Mansourizadeh and Javadi Azad[76] blended PES with CA to separate oil from water, and the process achieved stable flux of 27 L · m⁻² after 150 min using the blended membrane, and the pure PES membrane achieved stable flux of 7 L · m⁻² after 60 min, demonstrating significant flux enhancement caused by increased membrane hydrophilicity. Although blending modification is a simple and good method to improve membrane hydrophilicity, the main disadvantage of it is

TABLE 1 Classification of different types of membrane modification

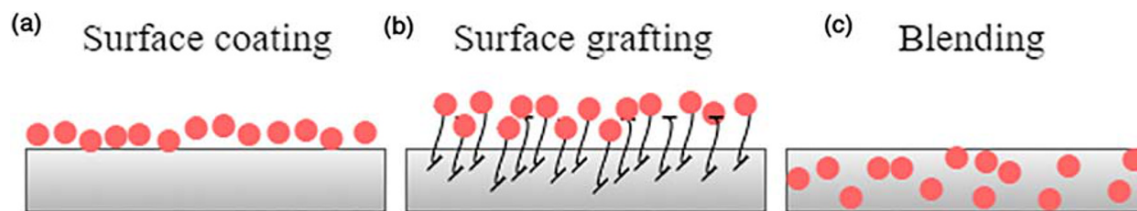|	Surface modification after membrane preparation			Membrane modification during membrane preparation	
	Surface coating	**Plasma treatment**	**Surface grafting**	**Bulk modification**	**Blending modification**
	Deposition of hydrophilic layer	Introduction of different functional groups	Chemical attachment of hydrophilic monomers	Incorporation of hydrophilic functional groups	Incorporation of hydrophilic materials
	Physical immobilization → Dipping, spraying, or direct adsorption of hydrophilic layer	Anchored layer → Coating with a hydrophilic layer + chemical treatment	Formation of covalent bonds between hydrophilic monomers and membrane surface	Addition of substituent groups in order to enhance bonds	Addition of hydrophilic or amphiphilic polymers into the host polymer / Addition of hydrophilic nanoparticles into the host polymer
Examples	Coating materials: - Glycerol - Poly (sodium 4-styrene sulfonate) - Polyvinyl alcohol - TiO_2 - SiO_2 - etc. Used chemical treatments: - Sulfonation (H_2SO_4, SO_3, etc.) - Crosslinking	Gas ionization methods: - Microwave - Radio frequency wave Ionized gases: - H_2O - CO_2 - O_2 - H_2 - He - Ne - N_2 - etc.	Grafting methods: - UV radiation - Plasma treatment - γ-ray - Electron beam radiation - O_3 Grafted monomers - Poly (ethylene glycol) methyl ether methacrylate - Poly(2-hydroxy-ethyl methacrylate) - etc.	- Sulfonation (H_2SO_4, SO_3, etc.) - Carboxylation (dry ice)	- Polymethyl methacylate - Sulfonated polycarbonate - Sulfonated polyether ketone - Polyethylene oxide - Branched co-polymers - etc. - Al_2O_3 - TiO_2 - SiO_2 - Fe_2O_3 - Carbon nanotubes - Composites - etc.

FIGURE 2 Schematic of different polymeric membrane modification methods

the fact that only a limited amount of particles remain on the membrane surface, because a large amount of them are retained in the bulk material, reducing the efficiency of the modification.[113]

For the treatment of oily wastewater, many studies have attempted to enhance membrane permeability and anti-fouling properties for both ceramic and polymeric membranes. However, there are several technical difficulties with ceramic membranes due to the difficulty of manipulating them.[26] Microscale tests show good progress and results, which facilitate commercialization.[20] The fabrication of membranes with structures composed of nanomaterials may revolutionize the purification of oily wastewater by making it more effective and economic.[6]

4.5.3 | Utilization of nanoparticles for membrane modification

The use of nanomaterials to modify membranes is increasing because of their large surface area and abundant functional groups that can change pore structure, produce desired membrane structures, ensure uniform coating, increase hydrophilicity, control membrane fouling, and contribute to achieve higher fluxes and rejection rates.[6,26,76,108,114] The addition of nanoparticles has effects on the morphology and physicochemical properties of the resulted membrane, being able to modify significantly not only the hydrophilicity of the membrane but also its porosity, charge density, and stability.[115] There are numerous studies about the optimum nanoparticle amount that can be added to the membrane; however, this value depends on several points: the materials of the membranes and their combinations, the modification method, the characteristics and effective dispersion of the nanoparticles, the conditions of the process, etc.[115–117] Numerous studies show that a small layer of nanoparticles can be beneficial due to the enhancement of membrane hydrophilicity; however, it can reduce the pore size, which can be acceptable until a certain level, but higher contents of the material can both reduce drastically the pore size and increase the agglomeration, blocking the pores for further water treatment.[117–121] The

method of nanoparticle addition, for example, coating, grafting, or blending, also alters the effect on the pore size. Typically, coating and grafting do not affect significantly the structure of the membrane, but blending can change the structure resulting in smaller losses[78,116,122]; moreover, it leads to more porous membrane structure in general.[115] Zhou et al.[123] coated an Al_2O_3 ceramic MF membrane with nano-sized ZrO_2 to treat oil-water emulsion and found that the nano-coating reduced the thickness of the fouling layer and increased oil repulsion, helping to wash out the oil droplets—even after they had adhered to the surface—thus enhancing flux recovery. The nano-coating also improved the hydrophilicity of the membrane, achieving a steady-state flux at 88% of the original flux, and the neat membrane ensured only 30% of the original flux. Karimnezhad et al.[124] tested three different nanomaterials to coat a Kevlar fabric membrane: para-aminobenzoate alumoxane (PAB-A), boehmite-epoxide, and polycitrate alumoxane (PC-A), according to a three-step dip-coating protocol. They found that the adhered oil droplets could easily be washed away with hot distilled water and acidic solution, recovering 89% of the original flux, due to the high hydrophilicity of the nanomaterial coatings.

It is also possible to coat a previously grafted membrane with nanoparticles. Liang et al.[113] grafted a PVDF UF membrane with poly (methacrylic acid; PMMA) by plasma-induced graft copolymerization, thus anchoring carboxyl groups on the silica nanoparticles. The fabricated membrane had high hydrophilicity, which resulted in two times higher flux and good antifouling performance, as 80% flux recovery was determined even after 3 cycles, with simple water rinsing. Song and Kim[125] fabricated UF membrane from PSf and poly(1-vinylpyrrolidone) grafted silica nanoparticle (PVP-g-silica) composite and observed 2.3 times higher flux with the modified membrane compared with the PSf membrane, which was explained by the good dispersion and adhesion of the nanoparticles onto the membrane.

Ahmad et al.[126] functionalized a PSf membrane by blending SiO_2 nanoparticles and enhanced the flux of oil-in-water emulsion from $1.08 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ (with the neat membrane) up to $17.32 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ with the modified membranes. As greater amounts of SiO_2 were used, more

improved antifouling properties were proved. The addition of SiO_2 also made easier to wash away the oil droplets. Krishnamurthy et al.[127] blended Cu_2O nanoparticles in PES membrane to treat oily water, and they found that with increasing nanoparticle amount, higher pore diameter, permeability, and anti-fouling properties (lower flux reduction) could be observed without jeopardizing the oil rejection. Leo et al.[128] treated oleic acid solutions with a blended PSf/ZnO membrane and detected higher hydrophilicity and lower flux reduction in the presence of the nanoparticle. There was an optimum at 2 wt.% of ZnO addition, where the highest permeability and the least fouling were determined. Higher amounts of ZnO resulted in severe agglomeration, jeopardizing membrane performance. Li et al.[129] found that when using PVDF membrane blended with nano-sized alumina particles in the case of oily wastewater treatment, it was possible to retain more than 90% of COD, improve flux by almost 100%, and completely regenerate the membrane after the backwashing of the modified membrane with 1% of OP-10 surfactant solution (pH 10). Metal-organic frameworks (MOFs) also appear to be an advantageous class of nanomaterials to be added to polymer matrices, because they enhance the filtration performance of both gas and liquid separation processes, as a result of their 2D structure and good morphology characteristics such as high porosity and surface area.[130,131] Gnanasekaran et al.[132] incorporated a Zn-based MOF in polymeric membranes (PES, CA, and PVDF) to treat hazardous wastewater, and they measured higher porosity (enhanced up to 10%), hydrophilicity (water contact angle reduced up to 14%), fluxes, and rejection rates (increased up to 20%) compared with the neat membranes, when the material was added to the system. Li et al.[133] decorated a PAN membrane with ammoniated zirconium dicarboxylate (UiO-66-NH_2) to treat different oil emulsions and found that the antifouling performance was outstanding, with great oil flux and rejection efficiencies, keeping its characteristics even after several water-cleaning cycles. Furthermore, MXene materials containing different metals (Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, etc.) also provide a new approach to be used in membrane filtration. They have the advantage of being 2D materials such as MOF; thus, they can be added as an ultrathin layer into the membrane, therefore enhancing the permeability and selectivity of the membrane.[134] In the publication of Tan et al.,[135] $Ti_3C_2T_x$ MXene was coated onto PVDF for a MD system, and the authors observed good fouling mitigation properties. According to Zhu et al.,[136] the application of 2D materials such as graphene, MOF, and MXene is essential to enhance membrane performance, and much more research is still needed into the use of these materials for water purification. Nevertheless, despite these advances, the application possibilities of nanomaterials to change membrane characteristics remains far from ideal to be widely used, and developments are still needed.[6] In this vein, membrane modification with photocatalytic nanomaterials has a huge potential and much research on this topic is being conducted to make it technically feasible.

5 | PHOTOCATALYTIC NANOMATERIALS FOR MEMBRANE MODIFICATION

Regular filtration shutdowns—to clean the membrane and recover the permeability—increase the cost and complexity of the membrane filtration system, whereas the use of chemicals reduce the membrane lifespan, produce highly contaminated wastewaters, and further increase the costs.[24] Based on this, the use of hydrophilic photocatalytic nanomaterials to develop membranes with antifouling and self-cleaning properties appears to be a promising technique, because these nanomaterials can decompose the fouling organic pollutants into small (or even nontoxic) substances—without the formation of secondary pollutants—by applying artificial or solar irradiation to activate them.[28–30]

Photocatalysts are semiconductors that can be activated by photons that have sufficiently high energy. These photons can originate from artificial (visible or UV) or solar irradiation.[137] In the activated nanoparticles an excited-state electron (e^-) of the valence band (VB) is transferred to the conduction band (CB), whereas a positively charged hole (h^+) is also generated in the process. These photogenerated electron/hole pairs can directly oxidize organic pollutants (or water/hydroxyl groups) and reduce an electron acceptor, such as a surface-adsorbed molecular oxygen (producing highly oxidative radicals, for example, $O_2\bullet^-$, $OH_2\bullet^-$, and $\bullet OH$). The photogenerated e^-/h^+ pair can also recombine with each other resulting in heat emission within a very short time (10–100 ns), thus losing their availability for further reactions (Figure 3).[138–140] As a result of these reactions, the organic compounds can be decomposed into harmless substances such as CO_2, H_2O and inorganic ions (sulfate, chloride, nitrate, etc.).[30,141]

To achieve these reactions, the redox potential of $\bullet OH/OH^-$ and $O_2/O_2\bullet^-$ couples have to be within the band gap of the given photocatalyst ($E°_{\bullet OH/OH^-} = 2.8$ V, $E°_{O2/O2\bullet^-} = -0.16$ V). The lower the band gap of the material, the less energy is necessary to move the electrons from the VB to the CB, which indicates the limits of the photoreactions (Figure 4).[142,143] Regarding these considerations, it is important to develop materials that
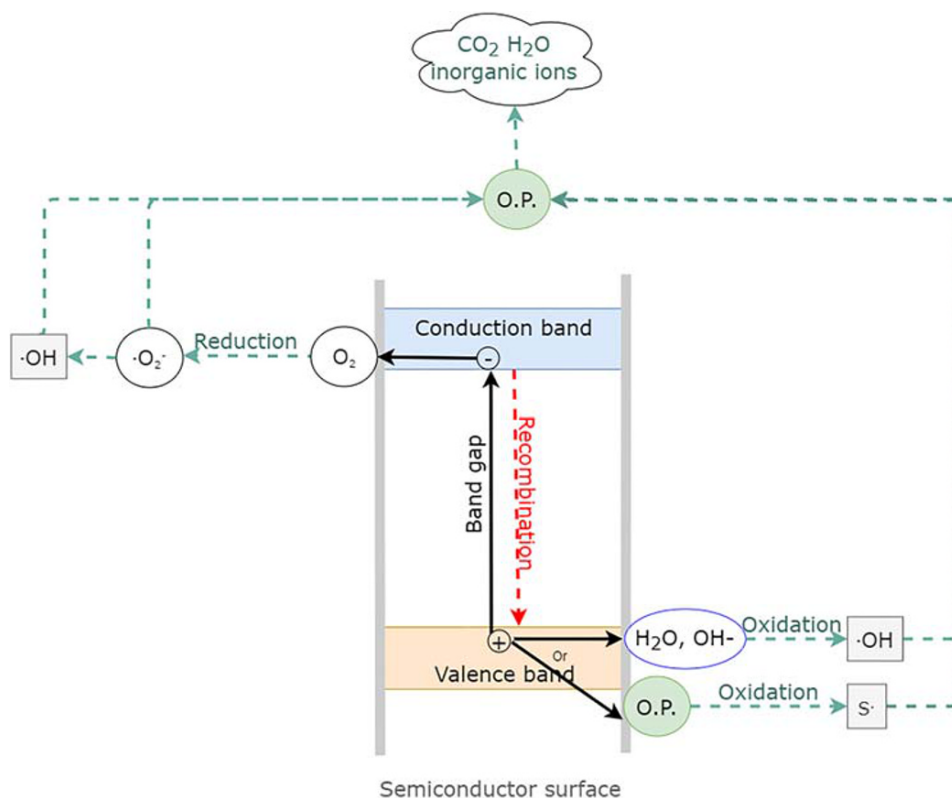
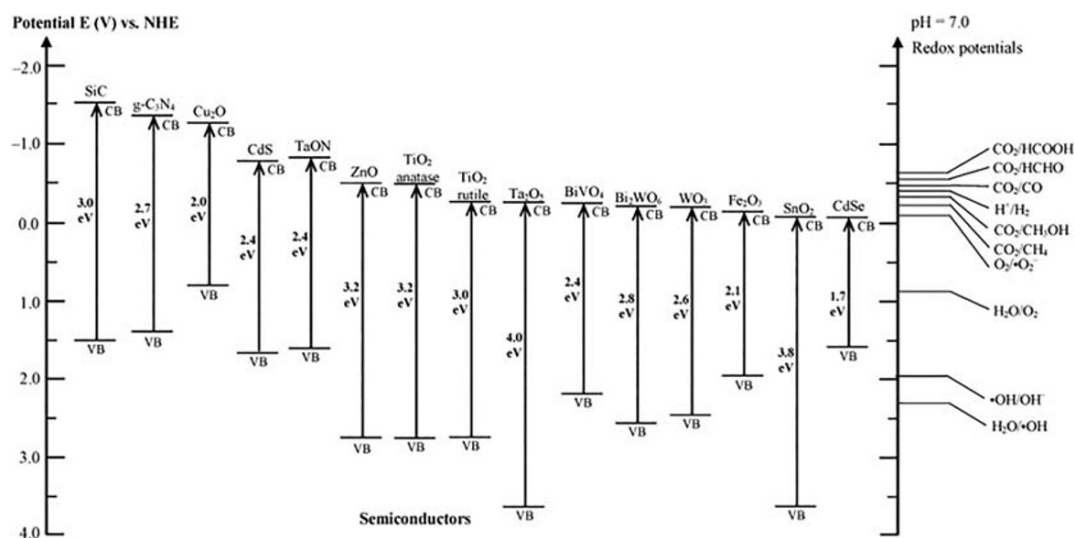**FIGURE 3** Mechanism of photocatalysis on a semiconductor's surface (O.P.: organic pollutants)


FIGURE 4 Band gap energies of various semiconductor photocatalysts[142]

have good photocatalytic activity, that is, low-energy requirement (lower band gap) and slow recombination of electron/hole pairs.[138]

Hybrid photocatalysts (nanocomposites) originate from coupling two or more semiconductors, which can help to enhance the photocatalytic activity. The system consists of semiconductors with different band gaps, and the incident photons lead to charge separation only in the material with the lower band gap, ensuring the lower energy requirement. Then this electron can easily be transferred to the CB of the other semiconductor (with the higher band gap), where it results in the reduction of a suitable electron acceptor (the adsorbed oxygen), and the oxidation takes place on the surface of the first semiconductor (Figure 5).[139] Due to this, the coupled material can result in the activity enhancement at different wavelengths, separate the e^-/h^+ pairs more efficiently and suppress their recombination. By using these kinds of composite materials for membrane modification a very promising technology can be created with great

FIGURE 5 Mechanism of photocatalysis in the case of composite semiconductors (O.P.: organic pollutants)
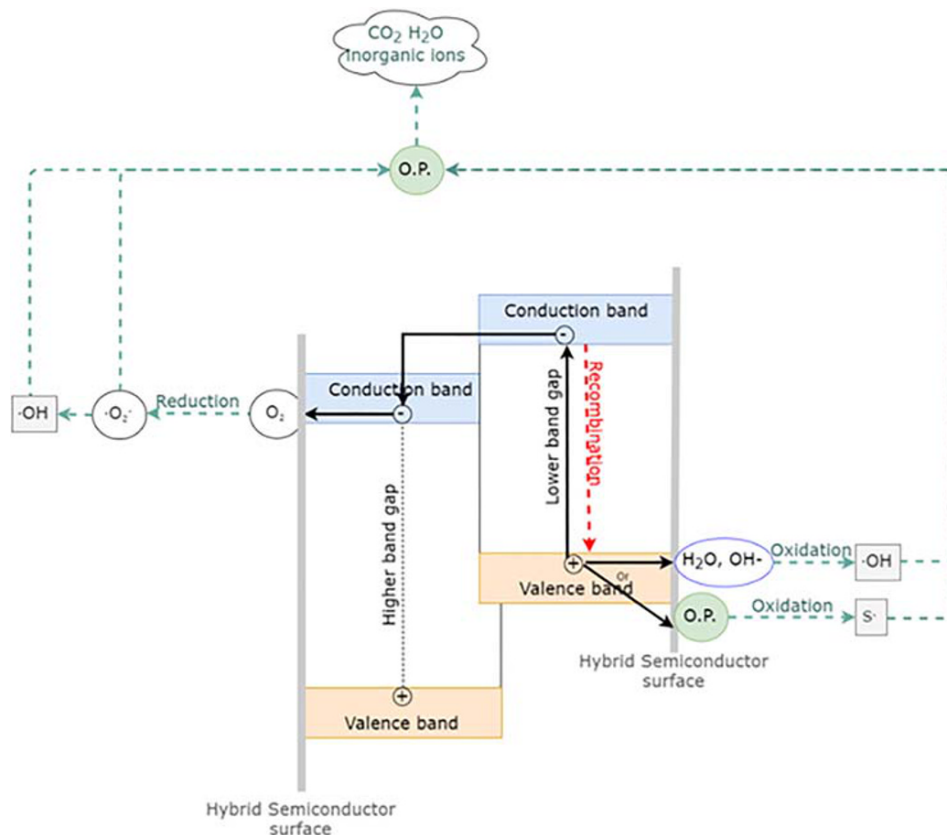
innovative possibilities in water and/or wastewater treatment.[118,144]

In general, photocatalytic wastewater treatment belongs to "advanced oxidation processes" (AOPs) the application of photocatalysts in membrane reactors (PMRs (photocatalytic membrane reactors)) can be immensely beneficial, which can be carried out in two main different ways: (a) with suspended photocatalysts (Figures 6b,c) and (ii) with photocatalysts immobilized on the membrane surface[117,145] (Figure 6a).

a In the case of the reactors with suspended catalysts, the aim of the treatment is the photocatalytic decomposition of the organic contaminants of the

wastewater, and membranes are used to eliminate/recover the nanoparticles. In suspension form, the photocatalysts have greater active surface area compared with immobilized catalysts, thus being able to degrade the pollutants with higher efficiency; however, the nanoparticles have to be separated and recovered, causing disadvantages such as contribution to fouling and flux reduction, decrease of photocatalytic performance, and additional time requirement.[117,118,138,145]

b Immobilized photocatalysts are used to enhance different properties of the membrane, like hydrophilicity and self-cleaning properties. These membranes can result in high purification performance, and with
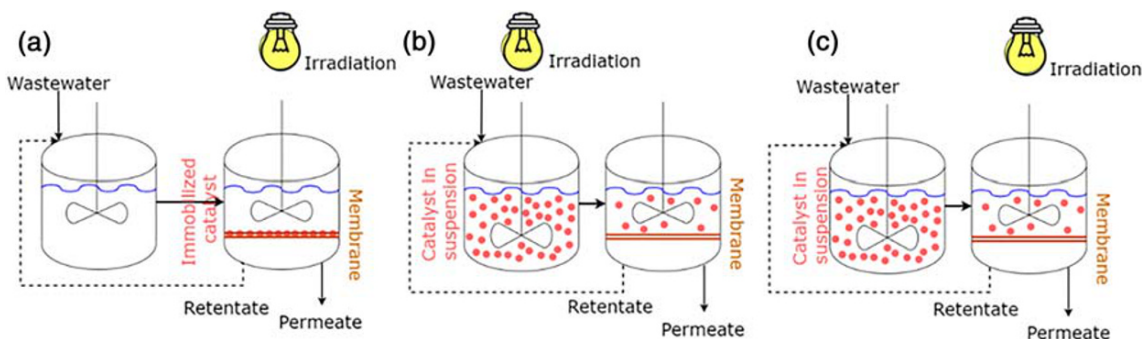

FIGURE 6 Schematic figures of the possible configurations of photocatalytic membrane reactors: (a) the catalyst in immobilized in/on the membrane; (b and c) the catalyst in suspension form

them, stricter discharge standards can be met. However, the main disadvantages are lower photocatalytic activity compared with the suspension method, and technical difficulties include irradiation of the membrane surface—which can be very difficult in case of continuous flow PMR system—and maintaining good dispersion and porosity of the particles on the membrane.[117,138,145]

In general, by using both kinds of PMR, it is possible to improve membrane self-cleaning properties, intensify organic decomposition, produce less sludge, and save chemicals. According to Molinari et al.[118] the suspension system is more effective in pollutant decomposition (compared with coated and blended membranes), and they also achieve three times higher efficiency by using immersed UV lamps instead of external lamps.

To be able to filter wastewaters with UV irradiated photocatalytic membranes, it is necessary to use membrane materials that remain stable with the chosen photocatalyst when exposed to UV irradiation and different radicals. Thus, the development of UV-resistant photocatalytic polymeric and ceramic membranes is an intensively investigated research area.[84,117,138,146]

In addition to this topic, photothermal materials can also be mentioned as they are also gaining attention concerning the decomposition of organic matter because they can bring double benefit: the use of solar energy to absorb photons (photochemistry) and the generation of heat (thermochemistry) to enhance the decomposition reaction rates. Photothermal materials enable the extended usage of the solar spectrum compared with pure photocatalysts—which are limited by their band gap.[147] These materials are required to have high solar absorption ability and small thermal emissivity; therefore, dark-colored heat-absorbing materials show great potential to be used as photothermal catalysts,[148,149] such as some metal oxides due to their thermal stability (e.g., CuO and Co_3O_4).[150] Carbon-based structures are also possible candidates to be used as photothermal catalysts due to their capability to convert light to heat, good thermal and mechanical stability, large surface area, low density, and high optical absorption rate (e.g., carbon quantum dots, graphene, and carbon nanotubes).[140,151] The reason that photothermal materials can be important in MD is that they can improve the decomposition of pollutants and improve the performance of the treatment while enhancing the thermal properties of the membranes thus, reducing heater energy input.[135,152]

For the development of photocatalytic membranes, investigations about the stability of possible membrane materials under UV irradiation and oxidative environment and about the stability of the nanomaterial on the membrane (to keep the filtration performance) are required. In terms of UV and oxidation stability, it is important to notice that there are numerous possible reactions that can occur between the polymer and the incident photons. Because photocatalysis produces oxidizing radicals, it is possible to trigger the degradation, functionalization, polymerization, or isomerization of a non-stable membrane. Therefore, the aim during the development of UV-stable photocatalytic membranes is to use such materials that do not deteriorate the original flux and selectivity of the membrane (thus retaining its pore structure) even under harsh conditions.[153,154] Chin et al.[154] investigated several different polymeric membranes (PVDF, PC, PS, PTFE, PP, PAN, PES, and CA) and concluded that PTFE, PVDF, and PAN membranes were stable even after 30 days of UV illumination. The same authors found that when they added nanomaterials to the system, the degradation of the membrane accelerated due to the oxidative compounds; they concluded that PTFE and PVDF had better performance in general, that is, UV and oxidation stability.

The modification method influences the stability of the material added to the membrane (Sections 4.5.1 and 4.5.2), and other important parameters affect its immobilization, such as type of the reactor (cross-flow or dead-end), type of membrane (e.g., flat sheet, plate, spiral-wound, tubular, and hollow fiber), conditions of the filtration (pressure, pH, time, temperature, stirring, etc.), and the characteristics of the used nanomaterial. Therefore, it is important to study and ensure the adherence of the nanoparticles to reach better filtration performance and to ensure that they are not leached or lost over time.[115]

Durability of the nanocomposite membranes is the most poorly investigated part of this research field, even though it is a key parameter to successfully scale up this technique. Some studies compare the mechanical stability of the modified and the neat membrane, and/or before and after the filtration/cleaning experiments.[78,106,120,155] Some studies also evaluate the membrane stability after their utilization under the UV-light-initiated oxidative conditions,[156–158] but researchers use a wide range of methodologies, for example, measure fluxes and rejection rates, analyze morphology (SEM, XRD or FTIR analysis), follow the changes of photocatalytic activity in time, or use simple physical analysis methods (e.g., turbidity and weight). For instance, Wang et al.[156] developed a ZnO-blended PVDF membrane and measured excellent stability during repeated filtration and UV irradiation for several (up to 15) cycles, and the flux and rejection rates were nearly constant. They also proved the stability of the modified membrane during oxidative conditions by measuring the ATR-FTIR spectra and water contact angle

before and after UV irradiation. A different approach was took by Kovács et al.,[78] who stirred water over the modified membrane and measured unchanged turbidity, thus confirming the stability of the immobilized TiO_2 nanoparticles. Du et al.[157] characterized both the membrane morphology and rejection rates and confirmed the stability of the modified membrane even after 20 cycles of filtration followed by solar irradiation. Liu et al.[158] analyzed the membrane by measuring the photocatalytic decomposition rate of the pollutant and calculated very similar values even after 5 cycles. In the case of blending modification, nanomaterial leaching mostly occurs during the membrane fabrication; therefore, the stability might be kept during its operation and the cleaning, resulting in an advantage in comparison to coating and grafting methods.[159,160] However, the analysis of membrane mechanical stability during long-term utilization would still be necessary. By using different methodologies, the comparison of results becomes difficult; therefore, it is very important to find standard methods that can be generally accepted.

Due to all of these concerns, it is worth mentioning that the membrane stability—UV, oxidation, and adherence—has to be studied in situ with the used polymer, without making general assumptions of the used materials.[115,138,154]

There are numerous well-known photocatalytic materials such as zinc oxide (ZnO), zinc sulfide (ZnS), tin oxide (SnO_2), copper oxide (CuO_2), cadmium sulfide (CdS), and tungsten trioxide (WO_3), but the most investigated is titanium dioxide (TiO_2), due to its multiple beneficial properties, such as high chemical stability, photocatalytic activity, availability, and low cost.[31,138]

5.1 | TiO_2-supported photocatalytic membranes

To produce self-cleaning membranes, the most relevant aspects of TiO_2 are its photocatalytic and hydrophilic properties that can be utilized simultaneously on the same surface even though the mechanisms are completely different.[143] To ensure the stability of the modified membrane under UV conditions, Chin et al.[154] investigated 10 different polymeric membranes. According to the changes in pure water flux, the release of TOC, and morphology analysis, the authors concluded that PTFE, PVDF, and PAN showed the greatest UV resistance if the membranes were coated with TiO_2, which results in additive oxidative stress (caused by the photogenerated reactive oxygen species). Molinari et al.[118] pointed out that commercial PAN, PSf+PP, and fluoride+PP membranes are also stable under UV light

when adding TiO_2 as photocatalyst. It is important to notice that the TiO_2 nanoparticle also affects the structure of the membrane, and thus, the performance of the filtration. Rahimpour et al.[122] compared blending and coating TiO_2 on a PES membrane and found that blending enhances porous structure, and both methods enhance antifouling properties and flux stability, even though the initial fluxes were smaller.

Bae and Tak[161] produced TiO_2-coated and TiO_2-blended membranes, by using three different membrane materials: PSf, PVDF, and PAN. They filtered activated sludge in a membrane bio-reactor system and found that regardless of the applied polymer, the nanoparticles reduced membrane fouling and improved filtration performance, by achieving higher initial and steady-state flux—even after longer periods—compared with the neat membrane. They also concluded that TiO_2 deposition resulted in higher fouling mitigation in comparison with blended TiO_2, because of the larger number of particles located on the surface of the membrane. Madaeni and Ghaemi[24] studied TiO_2-coated membranes to filter whey and achieved good photocatalytic and hydrophilic properties. They discovered that applying longer UV irradiation and more coating material can be beneficial to improve flux until the stable state is achieved. The addition of more photocatalyst then causes membrane blockage and, consequently, flux reduction. The use of TiO_2-modified membrane has numerous beneficial properties—such as the possibility to achieve higher fluxes and better self-cleaning properties—in the case of various types of wastewater, for example, dairy,[162,163] textile,[164,165] industrial,[119] agricultural[166] wastewaters, and also in the case of disinfection.[120,158] The investigation of its applicability to modify membranes for efficient oily wastewater treatment has gained attention in the last few years.[118,167]

Chang et al.[168] treated oil-contaminated water with TiO_2-coated ceramic membrane and detected the increase of flux by 150%, which was attributed to the enhancement of the surface hydrophilicity (water contact angle reduced from 33 to 8° due to the nanoparticle coating). Pan et al.[169] used TiO_2 in a dynamic ceramic membrane to treat engine-oil emulsion, and the enhanced antifouling property was explained by the change of complete to intermediate pore blocking. Tan et al.[170] filtered oil emulsions with glass fiber filters coated with three different types of TiO_2 nanostructures. They observed high hydrophilicity and good oil repelling properties in all cases, and they managed to achieve easy cleaning as the recovery of the membrane was accomplished via several cycles of washing with water. The self-cleaning properties of the modified membranes were also compared using UV irradiation, and the 3D nanosheet-decorated TiO_2 nanowire

had the highest photocatalytic activity among the three different investigated materials, completely recovering the superhydrophilic property of the membrane. Gondal et al.[171] created TiO$_2$-coated stainless-steel meshes by spray coating and used them to treat oil-in-water emulsions by gravity driven separation. The authors found that the superhydrophilic and underwater super-oleophobic membrane facilitated the replacement of oil with water, even when it was imbibed into the porous coating, improving antifouling properties and minimizing the fouling of the mesh.

Shi et al.[172] directly grafted TiO$_2$ onto PVDF membrane using a novel method and achieved high hydrophilicity—as the measured water contact angle reduced from 123 to 32°—and good antifouling properties (simple water washing was enough to completely regenerate the oil emulsion flux even after several cycles). They also proved the stability of the modified membrane under acidic, salty, and physical but not under alkaline environment. Kovács et al.[92] used TiO$_2$-coated PVDF membrane for the membrane filtration of a model oil-in-water emulsion (c_{oil} = 100 mg/L) and concluded that the catalyst reduced both irreversible and reversible resistances, and the oil retention was similar for both neat and coated membranes (96 ± 2%). However, in the case of the photocatalytic membrane, after rinsing it with distilled water, nearly the total flux was recovered. They observed the destabilization of the photocatalyst coating when the salt content of the oil-in-water emulsion was high, drawing attention to the limitations in the case of physical deposition. Venkatesh et al.[121] fabricated a hydrophilic membrane by blending a PVDF mixed matrix membranes with a one-dimensional (1D) PANI/TiO$_2$ nanofiber, in order to use it for the filtration of synthetic oil-in-water emulsion. The contact angle of water reduced as more nanomaterial was used, and the water flux increased from 80 to 132 L · m^{-2} · h^{-1}, and excellent antifouling properties were achieved, with 99% of oil rejection. Kovács et al.[78] prepared a TiO$_2$-deposited PAN membrane that did not leach during the filtration of oil-in-water emulsion and membrane cleaning. They also recorded good antifouling properties, higher flux, and better flux recovery with the modified membrane. Moslehyani et al.[173] developed a hybrid system to treat real petroleum refinery wastewater: a TiO$_2$-based photoreactor, which was used to oxidize the organic matter, followed by membrane filtration with a blended PVDF/multiwalled carbon-nanotube-modified membrane, which was responsible for separating the oxidized matter and the photocatalyst from the water. The photoreactor decomposed over 90% of the oil after 6 hr of UV irradiation. The modified membrane rejected more than 99% of the TiO$_2$ and the pollutants. Based on this

study, a PMR is a promising method for oily wastewater treatment, which shows high performance in the degradation of hydrocarbon compounds.

Numerous authors pointed out the "nontoxic" characteristics of TiO$_2$, regarding it many times as an environmentally friendly material that keeps its characteristics even when it is used in composites.[174,175] Nowadays, several studies show that TiO$_2$ can be harmful to both humans and the environment when released out of the system—in air, soil, or water.[174–177] Due to its potential risks, it is crucial to ensure its fixation, stability, and permanence on the material, avoiding its leaching and improving both the performance and safety of the treatment.[174] Despite all the advantages of using TiO$_2$, there are still not any commercial, photocatalytic membranes on the market. TiO$_2$ can only be activated efficiently using UV photons, which represents a small fraction (3.5–8%) of the total solar spectrum[33,178]; thus, solar systems that use TiO$_2$ have limited efficiency in the degradation of hydrocarbons.[32] Considering this and the fact that UV activation needs significant electrical energy, the development of visible-light active photocatalytic materials and their use in the preparation of photocatalytic membranes has a huge potential to achieve high-efficiency pollutant removal and/or membrane surface cleaning via the most environmentally friendly way: using natural sunlight for activation.[24,116,119,163,164] Solar light active superhydrophilic photocatalytic membranes could be the future's novel solution for advanced oil-in-water emulsion separation as they could be able to minimize the fouling problems, and be cleaned in a chemical- and energy-free way, by simple solar light irradiation. Due to this, a great number of new photocatalysts have been synthesized as possible alternatives to combine or substitute TiO$_2$, mainly as composites, by coupling two or more semiconductors. In the end, both the photocatalytic activity and the stability of the resulted photocatalytic membrane must be enhanced and ensured.

5.2 | Novel photocatalysts for photocatalytic membranes and future perspectives

There are two main directions in photocatalyst development: (a) to increase the visible light activity, and therefore solar light utilization efficiency by achieving lower band gap values (by TiO$_2$ modification or by the development of other photocatalysts), and (b) to reduce the recombination rate of electrons and holes by the preparation of composite materials in order to achieve higher photon utilization efficiency independently of the applied wavelength.[138]

For example, carbon nanotube (CNT) or halloysite nanotube (HNT) as composite components can enhance the photocatalytic efficiency of TiO_2 by preventing the recombination of e^-/h^+ pairs produced by TiO_2 under UV irradiation.[1,129,173,179,180] The addition of tungsten trioxide (WO_3) can also enhance the photocatalytic activity of TiO_2 by reducing the recombination rate of e^-/h^+ pairs, and it can result in increased visible light activity.[141,180,181] Some studies show that the deposition of silica, zeolite, clay, or even noble metals such as gold (Au), platinum (Pt), palladium (Pd), copper (Cu), and silver (Ag) nanoparticles onto TiO_2 can both increase the photocatalytic properties and prolong the lifetime of charge carriers; however, the properties of the noble metal should be studied carefully because it can affect the photocatalytic activity.[129,139,181–184] The use of composites containing cadmium sulfide (CdS), silicon dioxide (SiO_2), zirconium dioxide (ZrO_2), or zinc oxide (ZnO) is also beneficial in terms of the efficiency of organic pollutant decomposition with UV and even with visible light.[24,29,183,185] Bismuth vanadate ($BiVO_4$) is also being investigated as an option for a Ti-free semiconductor photocatalyst and was synthesized in many different morphologies such as spherical, T-shaped, and rod-like. Most of the research shows that $BiVO_4$ has great photocatalytic efficiency using visible light irradiation.[33,186–189] Reduced graphene oxide is also widely researched due to its high photothermal effect and its capability to keep and redirect the photogenerated electrons, which can improve the pollutant adsorption and light absorption efficiency.[151] Reduced graphene oxide can also be used in composite with TiO_2, improving both membrane hydrophilicity and photocatalytic activity, due to its good stability, conductivity, and optical properties.[190,191] Regarding the subject, it is worth highlighting that Pan et al.[192] reported an environmentally friendly in situ method to regenerate graphene by the electrochemical desorption of adsorbed pollutants, which might be a promising approach worth investigating in the field of TiO_2/graphene-based nanocomposite membranes. Some studies also include investigations about the stability of the nanocomposites even after several cycles of photocatalytic treatment, for example, TiO_2 with Pt and Ag as nanocomposite,[177] TiO_2 polymeric composites,[193] $BiVO_4/TiO_2$ nanocomposite,[194] and TiO_2/bentonite nanocomposite.[182]

Apart from the already established beneficial effects of adding MOF to polymer matrices, it is also possible to use it to improve the photocatalytic efficiency due to its ability to improve light harvesting, e^-/h^+ separation, and surface redox reaction.[195] Mohaghegh et al.[196] synthesized a hybrid nanocomposite consisting of $Ag_3PO_4/BiPO_4$, graphene, and copper terephthalate MOF and used it to photodecompose a herbicide. This material proved to have good photocatalytic activity under both UV and visible irradiation. Du et al.[157] fabricated a MOF-photocatalytic membrane consisting of UiO-66-NH_2(Zr/Hf) and used it to remove a toxic heavy metal ion (Cr (VI)) under sunlight irradiation. The material was stable with excellent performance because the porosity, flux, and rejection of the membrane were enhanced simultaneously, and it was possible to reuse the membrane with up to 94% removal efficiency even after 20 cycles. According to Li et al.,[134] the development of novel MOF-based membranes for liquid separation with photocatalytic characteristics will definitely be explored, even though the literature about it is scarce.

Although all of the mentioned research shows the enhancement of the nanocomposite's photocatalytic activity—with or without TiO_2—it is imperative to study the stability of: (a) the nanoparticles in the nanocomposites, (b) the nanocomposites in the membranes, and (c) the membrane under oxidation and UV (or solar) irradiation, for reasons already mentioned in this paper, while retaining the membrane performance.

Despite all the efforts to develop more efficient and/or visible/solar light active photocatalysts, most of the cited studies used the photocatalysts in suspension form and, in some cases in immobilized form. Many of them did not consider the possible enhancement of membrane performance. However, there are an increasing number of recent studies focusing on the possibilities of this topic, and many of them focus on oily wastewaters. TiO_2-composite membranes and TiO_2-free visible-light active membranes—prepared by both surface coating and blending processes—have also been investigated to simultaneously improve the decomposition and filtration performances (Table 2).

6 | DISCUSSION

As the usage of TiO_2 by itself did not prove to be worthwhile enough due to its already discussed shortcomings and based on the mentioned references in Table 2, a discussion can be held about how these advanced photocatalytic membranes with nanocomposites can significantly improve the flux, mitigate the fouling, and enhance the rejection rate and decomposition ratios.

Based on the Table 2 references about novel photocatalytic membranes to treat oily wastewater, some important considerations are as follows:

- The interaction between the nanocomposite and membrane can differ completely depending on the chosen materials and result in modified membranes that differ in their hydrophilicity, pore size, contact angle, etc.

TABLE 2 Comparison of different photocatalytic membranes to treat oil-contaminated water

Reference	Photocatalyst	Reactor	Light	Membrane	Method	O/w emulsion	C (mg/L)
199	TiO$_2$ + HNT	Photoreactor (TiO$_2$) + filtration (HNT)	UVC	PVDF	Phase-inversion	Bilge water	200
175	TiO2 + MWCNT	Photoreactor (TiO$_2$) + filtration (MWCNT)	UV	PVDF	Phase-inversion	Petroleum refinery	100
106	TiO$_2$ + CNT	Filtration + photocatalytic cleaning	UV	PVDF	Physical deposition	Crude oil	100
208	RGO-Ag-TiO$_2$	Photocatalytic membrane	Visible	CA	Physical deposition	Diesel	10000
200	HMO-TiO$_2$	Filtration + photocatalytic cleaning	UV	PES	Phase-inversion	Crude oil	500 and 2000
157	TiO$_2$/Fe$_2$O$_3$	Filtration + photocatalytic cleaning	UV	CA	Physical deposition	Cooking, olive, lubricant	2000
209	CeO$_2$	Filtration + photocatalytic cleaning	UV	St.Steel	Physical deposition	Hexadecane	-
193	SGO + TiO$_2$	Filtration + photocatalytic cleaning	UV	CA	Physical deposition	Toluene, crude, vegetable, diesel	10000
210	WO$_3$ or ZnO	Filtration + photocatalytic cleaning	UV	St.Steel	Physical deposition	Octane, hexadecane, olive	-
205	RGO/PDA/g-C$_3$N$_4$	Photocatalytic membrane	Visible	CA	Physical deposition	Diesel, gasoline, soybean	10000
201	TiO$_2$ + g-C$_3$N$_4^+$	Filtration + photocatalytic cleaning	Solar light	CA + GO (interlayer)	Physical deposition	Soybean	100
206	TiO$_2$+Ag	Photocatalytic membrane	UV	CA + SGO (interlayer)	Blending + deposition	Toluene, gasoline, heptane, chloroform	100
202	K-B-B-TiO$_2$	Filtration + photocatalytic cleaning	Visible and UV	PES	Phase-inversion	Biologically treated palm oil	COD 5000
207	ZIF-8/GO	Photocatalytic membrane	Visible (Xe lamp)	PVDF	Grafting + physical deposition	Toluene	30

TABLE 2 Continued

Reference	P (bar)	Neat/Modified	Flux–oil (L m^{-2} · h^{-1})	Flux–pure water (L · m^{-2}vh^{-1})	Rejection ratio (%)	Water contact angle (°)
199	0.2, 0.4, 0.6, 0.8	Neat / Modified:	37.2, 38.4, 40.0, 42.0 / 72.1, 79, 86, 95	– / –	98, 97,5 97, 96 / >99	78.13 / 47.35
175	1.0	Neat: / Modified:	2 / 40, 51, 62, 69[a]	– / –	43.2 / 92,3, 8.8, 9.4, 99.9[a,c]	67.2 / 52.1, 49.3, 42.9, 37.4[a]
106	1.0	TiO$_2$: / Modified:	– / –	– / –	92.5 to 94 (0 to 120 min) / 92.5 to 95 (0 to 120 min)	57.2 / 0, 0

TABLE 2 (Continued)

Reference	P (bar)	Neat/Modified	Flux–oil (L m⁻² · h⁻¹)	Flux–pure water (L · m⁻² vh⁻¹)	Rejection ratio (%)	Water contact angle (°)
208	Vacuum filter	Without light:	30 (1 cycle), 10 (cycle 6)	20472	98 (1 cycle), 97.5 (6 cycle)	66.31
		With light:	33 (cycle 1), 29 (cycle 6)	250, 220, 191, 100[a]	98.5 (1 cycle), >99.5 (6 cycle)	58.94, 42.78, 36.67[a]
200	1 bar	Neat:	–	21.2	98.16	69 to 15 in 65 seg
		Modified:	–	23.7, 28.5, 25.1, 27.3, 43.4[a]	98.57, 98, 97, 90.79[a]	to 15 in 3s, 22.5, 8.5 seg
157	Vacuum filter	Neat:	–	-	–	>100
		Modified:	81	-	–	After UV <10
209	Vacuum filter	Neat:	–	-	–	0
		Modified:	17	-	>99	150[e]
193	Vacuum filter	Neat:	–	-	–	–
		Modified:	84	-	>99.9	0
210	Gravity	Neat:	–	-	–	–
		Modified:	–	-	>99[d]	ZnO: 50.7, WO3: 16.4
205	Vacuum filter	Neat:	–	15	–	–
		Modified:	22 (without light), 25 (with light)	22, 40, 80[a]	98	Increases
201	0.5	Neat:	101	–	–	70 to 67.5 in 60 seg
		Modified:	347, 1085, 2507, 4536, 1397[a]	–	>99.9	65 to 43 in 60 seg
206	Gravity	Neat:	≈ 60 (after 10 cycles)	–	–	–
		Modified:	172, 82, 53[b]	–	>99	Reduced 10
202	4.0	Neat:	9.8	9.7	COD 72	63.2
		Modified:	14.5, 19.4, 17.9[a]	19.1, 37.3, 27.2[a]	COD 80.3, 88.7, 85.4[a]	57.5, 52.6, 50.6[a]
207	0.14	Neat:	65	53–64	–	70
		Modified:	95	188	~93	45 without light, 25 with light

Abbreviations: C: concentration of oil; CA: cellulose acetate; CNT: carbon nanotube; HMO: hydrous manganese oxide; HNT: halloysite nanotube; MWCNT: multi-walled carbon nanotube; O/w: oil in water; P: applied pressure; PES: polyethersulfone; PVDF: polyvinylidene fluoride; RGO: reduced graphene oxide; SGO: sulfonated graphene oxide; St.Steel: stainless steel mesh; ZIF: zeolitic imidazolate frameworks.

[a]As the content of the nanocomposite increases,
[b]As the pore size decreases.
[c]TiO₂ rejection (not oil).
[d]However, with ZnO the pore has to be smaller (max 50 µm) while with WO₃ it can be 150 µm.
[e]Hydrophobic membrane—the oil pass through.

- There are multiple methods of composite preparation and membrane modification, and they affect both membrane performance and photocatalytic activity.
- It is important to study the wastewater-membrane, wastewater-photocatalyst, and photocatalyst-membrane interactions, because sometimes the nanocomposites can also be considered as a source of fouling and affect membrane performance.[197–200]
- The concentration of the oil, oil droplet size, ionic strength, and the type of the oil-in-water emulsion[199] can strongly affect the measured fluxes, rejection rates, and fouling types.
- Operational conditions—pH, time, transmembrane pressure, cycles, cleaning, etc.—also result in different filtration and photocatalytic performances.[78,117,128,199–201]
- The presence of nanocomposites can be beneficial for the flux and anti-fouling properties until an optimal amount from which it can start to jeopardize membrane performance, for example, by reducing hydrophilicity, enlarging pore size, reducing rejection rate, increasing fouling layer, reducing flux, etc.[106,197,198,200]
- Membrane regeneration can be almost complete as it was observed in most of the cited studies, because flux recovery was often ∼100%, even after several cycles.[155,191,199,200,202–204]
- Photocatalytic properties are often characterized by dye (e.g., methylene blue) decomposition, due to its relatively fast degradation and the relative ease of the analytic method, as it can be measured by a spectrophotometer. Photocatalytic experiments achieve ∼90% dye degradation in most of the referenced studies.[202,205–207]
- Simultaneously applied photocatalysis and filtration have some technical problems that need to be studied in detail, such as the distance between the light source and the membrane, the wavelength of the used light, and the optimal treatment time for the efficient decomposition of organic matter before its filtration.[202–205]
- Both membrane hydrophilicity and membrane oleophobicity have to be studied in depth in order to (a) prevent the permeation of oil droplets, (b) selectively separate water from the oil-water mixtures, and (c) minimize the adhesion of the oil droplets.[133,208]
- Most of the studies investigated photocatalysis followed by membrane filtration[173,197] or membrane filtration followed by photocatalytic cleaning.[106,155,191,198–200,206,207] There is a lack of research that combines decomposition and self-cleaning simultaneously.

- The membrane stability—both UV, oxidation, and adherence—has to be studied in situ without making generalizations about the used material.[115,138,154]
- Each nanocomposite offers different advantages and disadvantages, and its use depends on the chosen membrane material, reactor type, conditions, etc.
- All studies assume a promising future for these techniques, and the appearance of commercial applications of these advanced oil-water separation techniques.

Several studies reporting good anti-fouling and/or self-cleaning properties, high achievable fluxes, high photocatalytic activity (under different irradiation conditions), and/or good stabilities (during laboratory scale conditions) predict that the practical application of photocatalytic nanocomposite membranes is on the close horizon. However, even after numerous promising achievements, still several challenges need to be overcome for practical applications at large scale. These challenges have not been clearly emphasized and need more attention in future investigations:

a Nanomaterial leakage during the long-term application of the nanocomposite membranes is rarely investigated even in laboratory conditions (in some cases it is, but only for 5 to 20 cycles[156–158] not for weeks or months). For the description of the durability, generally accepted and standardized methods would be necessary to make the different investigations comparable.
b Large-scale production and application studies are also missing. Long-term stability experiments under practical conditions also need to be carried out.
c The examination of cost-effectiveness of different membrane fabrication methods and their applications would be required for the successful development of this technique.
d The efficient combination of beneficial surface properties, durability, high photocatalytic activity (even under solar irradiation), and cost effectiveness is also a remaining challenge.
e Finally, engineering challenges must also be taken into consideration, as the application of photocatalytic membrane surfaces that can be cleaned even with solar light requires unique solutions.

7 | SUMMARY

The effective treatment of oily wastewater is necessary because these wastewaters are produced in high quantities and oil discharge causes damage to the natural environment and endanger human health. To meet the stringent emission limits, conventional techniques such

as skimming, centrifugation, chemical destabilization, flotation, and biological treatment are not enough, because these methods are not able to remove small (submicron and nano-scaled) emulsified oil droplets. Membrane filtration plays an important role to complement the conventional treatment methods of oily wastewaters and to effectively remove these finely dispersed oils. There are different suitable types (MF, UF, NF, and RO) and materials (polymer and ceramic) of membranes; however, membrane fouling and flux reduction are still the major limitation to the application of these technologies.

In order to enhance membrane performance, stability, and antifouling properties, it is possible to modify the membrane by adding nanomaterials to its surface or by blending it with them. Superhydrophilic photocatalytic membranes are promising for the treatment of oil-contaminated waters because of their simultaneous efficiency in both degrading and separating organic pollutants from the feedwater, resulting in membranes with self-cleaning properties and good anti-fouling properties. TiO_2 has been widely used to degrade organic compounds; nevertheless, it is effective only under UV irradiation, which makes the system complex and/or not economically viable. Membrane modification with photocatalytic composite nanomaterials that can be activated with high efficiency by UV or even by visible/solar light is one of the options with a huge potential to (a) enhance membrane performance and antifouling properties, (b) be cost-effective, (c) enable chemical-free membrane cleaning, and (d) improve the degradation of pollutants, possibly by the utilization of a cost-free light source—the Sun. Besides, the development of efficient photocatalytic membranes also relies on the investigation of either the stability of possible membrane materials under UV irradiation and oxidative environment, or the stability of the nanomaterial/nanocomposite on the membrane.

The research based on the development of composite nanomaterials and photocatalytic membranes for these purposes has been increasing in the last few years, and the commercial application of this advanced oil-water separation technique is highly expected in the near future, but still several mentioned challenges need to be overcome for the practical applications.

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